VOLUME 77, NUMBER 6 PHYSICAL REVIEW LETTERS 5 AUGUST 1996

Site Exchange of Ge and Sb on Si(100) during Surfactant-Mediated Epitaxial Growth

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(Received 25 March 1996)

The bonding geometry of Ge and Sb on Si(100) is investigated using scattered MeV ion energy distributions with transmission ion channeling. Coverage of 0.15 monolayer (ML) and 0.68 ML of Ge deposited at room temperature (RT) on Sb-terminated Si(100) are studied, both before and after annealing at 350 °C. We find that RT deposition of Ge for both coverages is consistent with a model of loosely bonded Ge dimers adsorbed between undisturbed Sb dimer rows. After annealing, we observe bulklike Ge underneath Sb dimers for 0.68 ML Ge. Our results are compared to several models in the literature. [S0031-9007(96)00775-2]

PACS numbers: 68.35.Bs, 79.20.Rf, 79.60.Bm, 79.60.Dp

The use of surfactants in creating high quality heteroepitaxial films has been of interest for several years [1–2]. For example, surfactants such as As and Sb are well known to aid in creating high quality Ge/Si heterostructures. The low energy, stable termination that these elements provide causes an overlayer, i.e., Ge or Si, to be rapidly incorporated into the bulk. Such an inhibition of the surface diffusion of Ge or Si is the basis of the high quality heteroepitaxial films; islanding is prevented, and layer-by-layer growth is achieved. The fact that surfactant-mediated growth provides abrupt interface heterostructures is well documented [3–5]. However, the microscopic details of the site exchange processes between Ge/Si and the surfactant are not well understood, and, in fact, are debated in the literature [6–8].

Several models are available in the literature describing differing means by which the Ge/Sb site exchange occurs. Actually, the models discussed here are for As on Si(100), and we are considering Sb. As and Sb can be expected to behave in the same way here as (locally) they dimerize similarly on Si(100) (differences in behavior are readily attributable to the size difference of As and Sb) [9]. One model due to Tromp and Reuter [6] (referred to as the *Tromp model*) states that Ge arriving at the surface initially breaks the Sb dimers, forming rotated Ge dimers. As additional Ge dimers form in adjacent sites, a “two-dimer correlated exchange” occurs with the Sb. The total energy calculations of Yu and Oshiyama [7] (*Yu model*) describe a complex series of stages in which near-interstitial Sb is predicted, eventually leading, with a sufficient Ge coverage, to Sb on the surface. The final state itself, with Sb dimers on the surface and Ge in near-bulk sites (*final state*), has been determined experimentally [10,11]. In order to determine which path the Ge/Sb site exchange follows, one must prepare the system in its initial bonding state. This may be done using a low Ge coverage since the models suggest that a locally high Ge concentration is necessary for the transition to the final state. Further, energy and diffusion barriers may be exploited to freeze the system in its initial state by deposition at room temperature. These barriers can then be explored by annealing the sample to see if a transition to the final state can be observed.

In this Letter, we examine the microscopic site exchange mechanism that occurs in surfactant-mediated growth through a study of the system Ge/Sb/Si(100) [Sb coverage ~1 ML (monolayer), Ge coverage 0.15 and 0.68 ML]. The Sb was deposited first, followed by Ge at RT. Experimental scattered ion energy distributions were obtained for directions close to the ⟨100⟩ axis (the surface of interest on the beam-exit side of the crystal). A Monte Carlo simulation of channeling [12–15] was employed for the calculation of ion positions and energies as they exit the crystal. Simulated energy distributions were then calculated by taking adsorbate site locations from the literature and overlapping them with these ion positions (and corresponding energies). The experimental energy distributions were compared to the simulated energy distributions for predictions of the adsorbate sites prior to the final site exchange [6,7] as well as to a model for the final state configuration [10,11]. The sample was then annealed at 350 °C for 10 min to see if energetics and diffusion would lead to site exchange. The data before annealing are consistent with undisturbed Sb dimers on Si, with Ge in loosely bonded dimers, whereas after annealing, for the 0.68 ML Ge coverage, the final state fits the data best, showing the importance of energetics in surfactant-mediated growth.

A description of the experimental setup can be found elsewhere [11,16]. Sb was deposited on the clean, single-crystal Si window ($\sim 0.5\ \mu$m in thickness and 5–7 mm in diameter) from a boron nitride effusion cell [17]. The sample itself was held at ~ 500 °C and exposed to several monolayers of Sb to ensure saturation of the surface, ~ 0.85 ML [18] (1 ML = 6.78×10^{14} atoms/cm^2). The sample was then cooled to RT and placed in front of a Ge effusion cell, with an evaporation rate of ~ 0.15 ML/min. The Sb and Ge coverages were 0.80 ML and (0.15 and 0.68 ML), respectively, determined by Rutherford backscattering.

The sample was transferred under UHV to an ion scattering chamber (base pressure $\sim 5 \times 10^{-11}$ Torr) and placed on a two axis goniometer. A beam of 2.5 MeV He^{+} ions was produced by a 3.5 MV Van de Graaff accelerator and collimated to an angular divergence of 0.03°. Crystal alignment was performed in a transmission geometry, with the Ge/Sb on the beam-exit side of the sample, "by eye" by viewing the transmitted beam on a piece of quartz at the end of the beam line. By monitoring the Si yield and comparing with simulation, the accuracy of this procedure is estimated to be 0.02°–0.05°. Good approximations to "random" directions (directions where energy losses are close to those in amorphous media [19]) were found by comparing mean energy loss to random energy loss in simulated spectra over a large range of tilt and azimuth [16]. Experimental energy distributions were obtained at three different crystallographic directions, $(\theta, \phi) = (0^\circ, 0^\circ)$, $(\theta, \phi) = (6^\circ, 45^\circ)$, and $(\theta, \phi) = (6^\circ, 30^\circ)$, where θ is the tilt from the $\langle 100 \rangle$ and ϕ the azimuth relative to the $\{100\}$. These directions are, respectively, the $\langle 100 \rangle$ axis, the $\{100\}$ plane, and "random" incidence. Comparison of the random incidence data with simulation was used to determine the Si substrate thickness.

Scattered ions were detected and energy analyzed by three ion-implanted, passivated solid state detectors located at scattering angles of 70°, 79°, and 150°. The energy distributions were each collected for 24 μC of the integrated beam current. This minimizes irradiation damage (axial channeling $\chi_{\min}$ increase of a few percent at double this dose) while maximizing the counting statistics for submonolayer adsorbate coverages. Irradiation damage is further minimized by aligning with the high symmetry directions first. All three were taken on the same beam spot to minimize adsorbate coverage and Si thickness variation. Finally, the experimental and simulated energy distributions were normalized to the random yield; for each distribution, the counts in each energy bin were divided by the total number of counts in the random distribution. After collecting data for the three crystallographic directions described above, the sample was annealed at ~ 350 °C for 10 min. Energy distributions as above were then obtained on a new beam spot. The Monte Carlo simulation program and how it can be used to create adsorbate site energy distributions is described elsewhere [11,16]. A linear background (fit to the experimental data) was assumed and added to the simulated energy distributions.

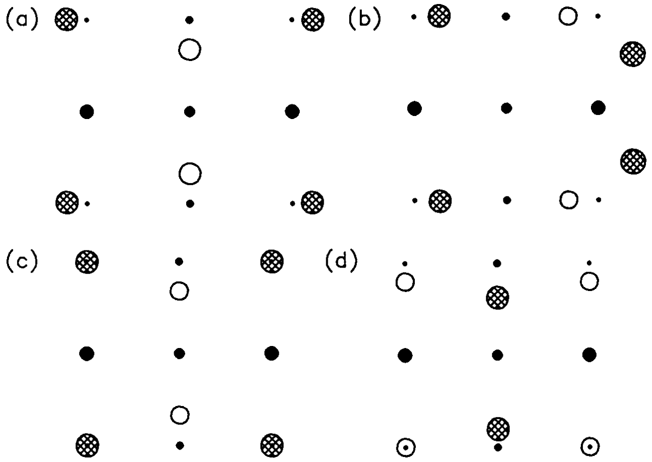

FIG. 1. View of the Si(100) surface from above showing the models tested in the paper: (a) Yu model B (Ge dimers between weakened Sb dimer rows), (b) Yu model C (interstitial Sb atoms), (c) Tromp model (Sb dimers broken by Ge), and (d) the experimentally determined final state. Black circles represent Si, with the size indicating proximity to the surface, open circles are Ge, and crosshatched circles Sb.

As discussed earlier, several models have been proposed for the initial stages in surfactant-mediated growth. The final state [10] is the experimentally determined Ge and Sb sites after the Sb has floated to the surface, incorporating the Ge into the bulk [Fig. 1(d)]. The Tromp model offers a possible initial bonding state in which Ge arriving at the surface initially breaks the Sb dimers, forming rotated Ge dimers [Fig. 1(c)]. At 0.15 ML coverage and assuming random Ge dimer site occupation, 80% of the Ge should not be able to undergo the two-dimer correlated exchange and the surface would be expected to be in this initial state. For 0.68 ML Ge coverage, the Tromp model would predict essentially all of the Ge to be in the final state. Note that the Tromp model assumes deposition at elevated temperatures and that the transition to the final state is driven by Ge coverage. Finally, the Yu model finds that Ge dimers bond initially between the Sb dimer rows [*Yu model B,* named for the figure in their publication, Fig. 1(a)]. They refer to this configuration as stable, but contend that it is energetically favored to pass to a state in which the Ge and Sb exchange sites, resulting in interstitial Sb dimers between the Sb dimer rows and subsurface Sb-Ge dimers [*Yu model C,* Fig. 1(b)]. Again, increasing Ge coverage facilitates a transition to the final state. Another model due to Ohno [8] would appear similar to the Tromp model in our technique.

For each of the above models, energy distributions for directions close to $\langle 100 \rangle$ were simulated and compared with the experimental data. The experimental directions were chosen as the most sensitive to the lateral location of the adatoms necessary for evaluation of the above models. Additional incidence angles would not have contributed much to this end, and would have reduced the incident dose acquired in the most sensitive orientations. Directions near additional major axes in silicon were also not necessary as a comprehensive site determination for this complex system would have been extremely difficult.

In simulating these models, the exact choice of adatom location is somewhat uncertain as they are not all well specified in the models (this excludes the final state which has experimentally determined sites). Coordinates had to be chosen for the adsorbates that would represent the models as closely as possible. For Sb dimerized with Sb or Ge, the channel position selected was the experimentally determined site for Sb dimerized with Sb on Si(100) [16]. For Ge dimerized with Sb or Ge, the experimentally determined site for Ge dimerized with Ge on Si(100) without a tilt was used [20]. The interstitial Sb atoms in the Yu model are specified. Further, substitutional-like atoms in the models were assumed to be exactly substitutional. This is perhaps unlikely (subsurface reconstructions are expected [21–23]), but displacements up to 0.4 Å from bulk sites were tested and not found to affect the conclusions. Finally, for each Ge coverage, excess Sb was assumed to be dimerized on Si(100) in the usual manner.

Figure 2 displays before and after annealing ⟨100⟩ axial aligned experimental data for 0.15 ML Ge coverage and how they compare with the final state (long dashed line), the Tromp model (short dashed line), and Yu model C (medium dashed line). Based on these fits alone, it is clear that neither the Tromp model nor the Yu model C fit the data well for either temperature. The same conclusions were evident for the {100} planar data, not shown (all models, of course, fit the random distributions). The final state provides a better fit in both cases. Thus, either the final state is already present at 0.15 ML Ge coverage and RT, which would contradict both the Tromp and Yu models, or an initial state not yet investigated is present.

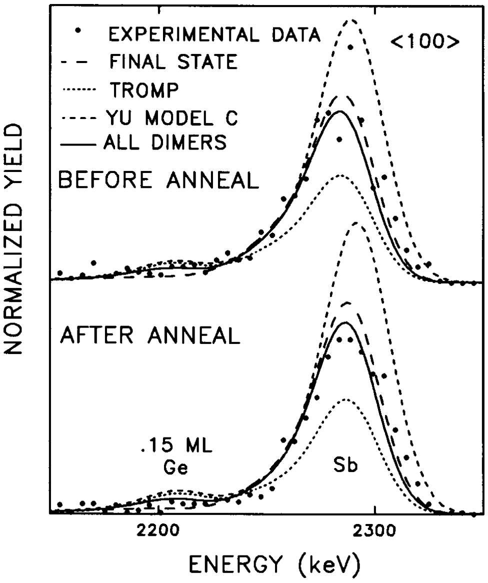

FIG. 2. Monte Carlo simulated scattered ion energy distributions (lines) for possible Ge and Sb sites for the system Ge/Sb/Si(100) (see text) compared with the experimental data (dots) for the ⟨100⟩ aligned direction (both before and after annealing). The Ge coverage is 0.15 ML. All spectra are normalized to the random yield (see text). Slight differences in simulations between before and after annealing are due to separate simulations for the different Si thicknesses (different beam spots). The shift in energy between Figs. 2 and 3 is also due to different Si thicknesses (different samples).

In Fig. 3, we show the data for a Ge coverage of 0.68 ML (Sb coverage unchanged). Again, neither of the discussed models fit the experimental data (nor would they be expected to at this Ge coverage). After annealing (but not before), the final state fits both peaks extremely well, showing a clear transition from some intermediate state to the final state. The solid curve represents a simple model where the Sb dimers on Si(100) [16] remain unbroken (and unaltered) when Ge is deposited. This model fits the unannealed Sb data very well. Further, for the unannealed case, if the Ge is assumed to dimerize on the surface, the same (surface plane) dimer bond length as Sb on Si(100) (2.80 Å) gives a good fit to the Ge data as well. We shall refer to this model as the *all dimer* model. It should be pointed out that the Ge need not actually dimerize, it must only be located in sites (relative to bulk sites) that mimic dimerization. Further, it is interesting that this model is similar to Yu model B. When Ge initially hits the surface, Yu *et al.* predict Ge dimerization between the Sb dimer rows accompanied by a weakening of the Sb dimers. However, we observe no weakening of the Sb dimers, and the Ge site that they propose does not fit the data shown in Fig. 3 (dimer bond length is too short). Based on our experimental data, it appears that the all dimer model is a metastable initial state that can readily undergo a transition to the final state upon annealing.

We are now in a position to test this model in our low Ge coverage data. Returning to Fig. 2, we see that the all dimer model (solid line) competes very well with the final

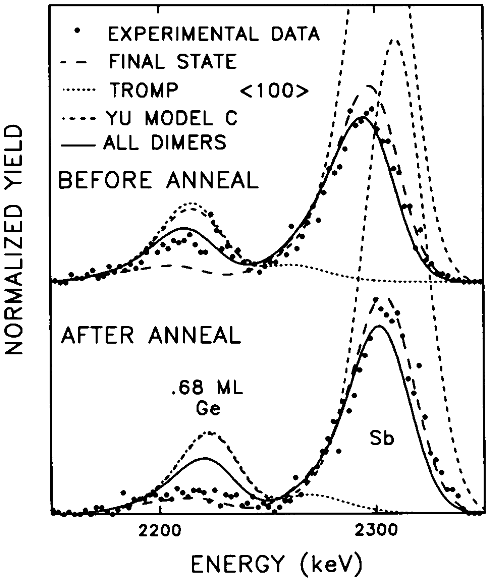

FIG. 3. Same as Fig. 2, but Ge coverage is 0.68 ML.

state. If this all dimer initial state offers a convincing fit to the data at high Ge coverage, then it would be expected to be present at low Ge coverages, and this is consistent with our unannealed data. In Fig. 2, it is not clear that a transition to the final state has occurred after annealing. The Ge data support a transition; however, the statistics are poor. Perhaps, as suggested by both the Tromp and Yu models, at low coverage the transition to the final state is kinetically prohibited. Note also that the final state model in Fig. 2 corresponds to full ML Ge coverage. Small islands of Ge in the final state may give slightly altered positions from those assumed, possibly explaining a poor fit [8].

In conclusion, the microscopic site exchange mechanism for the system Ge/Sb/Si(100) responsible for surfactant-mediated growth [*i.e.*, the transformation to Sb/Ge/Si(100) with the Ge occupying near-bulk sites] has been studied using scattered ion energy distributions. To isolate the system prior to the final site exchange, a low coverage of Ge was deposited at near room temperature. Experimental energy distributions were obtained for directions close to the $\langle 100 \rangle$ axis. A Monte Carlo simulation of channeling loss was employed for the simulation of energy distributions for predictions of several early stages in the site exchange process found in the literature.

It is found that an initial state similar to one proposed by Yu and Oshiyama (Yu model B) fits the data. We find, however, that room temperature deposition of Ge does not break or alter the Sb on Si(100) dimers, and the Ge itself is registered with the substrate, possibly in loose dimers with about the same dimer bond length as the Sb dimers. After annealing, the best fit to the data for 0.68 ML Ge coverage is consistent with Sb returning to the surface, incorporating Ge into the bulk, indicating the role of energetics in surfactant-mediated growth.

We gratefully acknowledge the technical assistance of R. Johns and D. McNeill. This work was supported by the NSF (DMR) and the University of Florida Division of Sponsored Research.

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